

## **METHODS FOR JOINING SILICON CARBIDE COMPOSITES FOR HIGH TEMPERATURE STRUCTURAL APPLICATIONS**

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### **OBJECTIVE**

Reliable and practical joining techniques are required to enable the use of silicon carbide composites in fusion energy systems. The variety of demanding criteria for the properties of joints will be described, including those pertaining to fusion energy systems. Issues concerning practical fabrication of joints will also be discussed. Preliminary results on the thermal stability of joints formed by a reaction based joining approach will be presented.

### **SUMMARY**

Joining methods are required to allow affordable fabrication of large or complex SiC/SiC components for fusion energy systems. Previous analysis of the criteria for successful and functional joints indicate that reaction-formed and polymer-derived silicon carbide should be considered as candidate joint materials. Efforts have been initiated to investigate the issues involved with fabrication and durability of these joints. This report summarizes initial investigations of the long-term thermal stability of silicon carbide joints formed by a reaction-based approach. Results indicate that the joint may contain unreacted phases that react further during high-temperature exposure. These results, and their implications, must be confirmed by additional investigations.

### **PROGRESS AND STATUS**

#### INTRODUCTION

The development of fusion energy systems creates many demanding criteria for the materials to be used in this application. One criterion, is the need for a hermetic material that can chemically and mechanically withstand high-temperatures and neutron fluxes as the "first-wall" material. In addition, the radioactivation of the material to be used as the first wall should be below the limits for a safe and environmentally benign lifecycle. A candidate material for this application is silicon carbide fiber-reinforced, silicon carbide (SiC/SiC). These composites possess desirable thermal, mechanical, and radiation stability. A limitation of these materials, however, is that they can only be produced in limited sizes and shapes. Therefore, to fabricate a complete fusion energy system a method of joining SiC/SiC components, without compromising the properties that are needed, is required.

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Since silicon carbide has many desirable properties for use as a "first-wall" in a fusion energy system [1-4], it is undesirable to use a joining technique that introduces dissimilar materials at the inner face of the first wall. In addition, to avoid poisoning the plasma the first wall must be hermetic. Thus, it is highly likely that a means of joining SiC/SiC components to each other is required. Two attractive methods of joining silicon carbide with other forms of silicon carbide have been developed: reaction bonding [5-8], and preceramic polymer adhesives [9-15]. In this paper, preliminary results obtained from joints formed by reaction based forming will be presented. Although other investigators have demonstrated that joints with required values of strengths can be formed [5-8], the long term stability of the joint, and consequent affects on the mechanical properties of the joint, require further attention. In this study joints were annealed under long term static and cyclic, high temperature conditions and the resulting microstructures were examined.

### Issues Concerning Joining for Fusion Energy Systems

The criteria typically required for successful ceramic-to-ceramic joints for high temperature applications are usually: (1) adequate mechanical properties, and (2) chemical stability with respect to the components being joined and with the service atmosphere. In addition to these basic requirements, materials for joining silicon carbide composites required for use in fusion energy systems must meet other criteria that assure that fusion energy systems produce economically viable power, and operate in a safe and environmentally benign manner over their lifetimes. Hence, any joining method used for fusion energy systems must also satisfy the conditions of radiation resistance, mechanical integrity, desirable thermal properties, safety during operation and maintenance, prevention of injuries in the case of accidental release, and environmentally benign waste disposal.

The requirements of safety, injury, and waste disposal have been considered from the perspective of identifying elements that form transmutation products, after exposure to fusion energy system operating conditions, that exceed the accepted limits [16,17]. From this point of view, several elements that may potentially be attractive for use in joining must be excluded. Nickel, molybdenum, niobium, and cobalt are unacceptable. In addition, since joining will occur at the construction site of a fusion energy system it is preferable that the joining technique be performed in the ambient environment without applied pressure. Furthermore, the temperature used for joining must be below that which causes degradation of the fibers: believed to be 1200-1400 C. The joining technique must be compatible with the other materials and processes used during assembly of the fusion energy system. Consideration of these factors has led to the selection of silicon carbide formed by two different methods as potential joining compounds: (1) reaction-forming, and (2) pyrolysis of preceramic polymers. In this report, however, only joints fabricated by reaction-forming will be discussed.

## **EXPERIMENTAL TECHNIQUE**

To evaluate the suitability of joints formed by the reaction-based forming approach, plates of monolithic silicon carbide (Hexoloy SA, Carborundum Co., Niagara, NY) were joined using the ARCjoinT technique [6-8]. Two plates of monolithic silicon carbide were cut into 25 mm-long by 4 mm-thick pieces. A carbonaceous mixture was applied to the ends of the plates that were to be joined and this was cured at 110-120°C for 10 to 20 minutes. Subsequently, a slurry of pure silicon powder was applied to the surface of the joint region and heated up to 1425°C for 5-10 minutes. Capillary forces drew the molten silicon into the joint region where it reacted with the carbon to form silicon carbide. The resulting joint material consisted of silicon carbide with controllable amounts of silicon and other phases as determined by the composition of the raw materials and infiltrant. A limited number of joints between pieces of silicon carbide composite material were also fabricated. This composite was reinforced with Hi-Nicalon fibers (Nippon Carbon Co., Yokohama, Japan) that had

been coated with a 1  $\mu\text{m}$ -thick layer of carbon prior to matrix infiltration via chemical vapor infiltration. In addition, an approximately 2  $\mu\text{m}$ -thick layer of silicon carbide was deposited on the outside of the composite to inhibit oxidation at high-temperatures.

The plates that were joined using the method described above were cut into bars that were 44 x 4 x 4 mm. The bars were cut so that the joint was at the middle of the bar and the plane of joining was aligned so that it was parallel to the applied load. Several of the bars were annealed in a resistively-heated, quartz-image, furnace under vacuum. A series of specimens was annealed at 1100°C for ten consecutive 10 h long cycles. The microstructure of untreated and annealed specimens was investigated via scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM).

## RESULTS

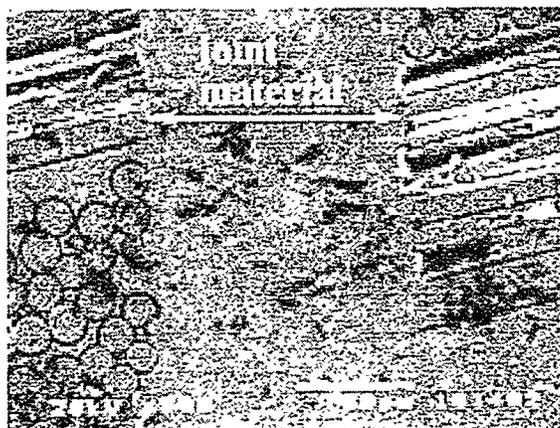


Figure 1. Micrograph of a cross section of two pieces of silicon carbide joined with reaction-bonded silicon carbide.

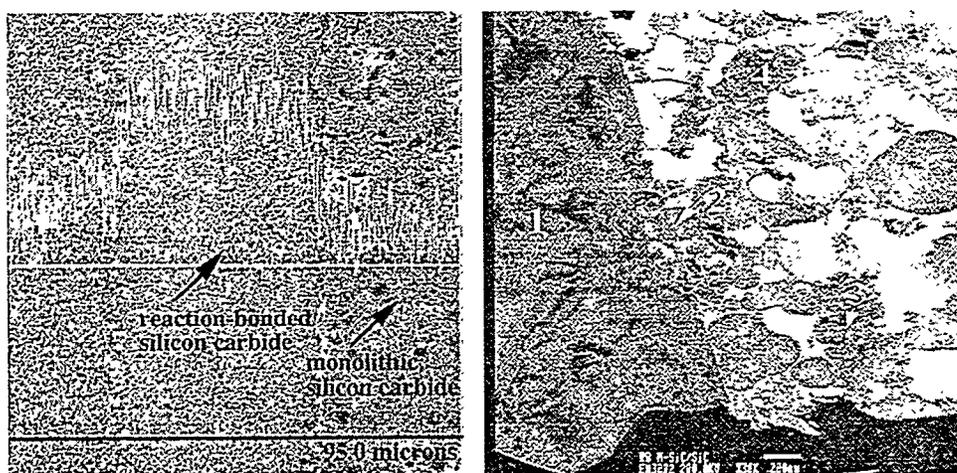


Figure 2. Micrographs of a cross section of two pieces of monolithic silicon carbide joined by reaction-bonded silicon carbide: (a) SEM image, with EDX signal from silicon superimposed, and (b) low magnification TEM micrograph. In (b), 1 indicates monolithic silicon carbide, (2) epitaxial carbon, (3) indicates reaction bonded silicon carbide, and (4) indicates a pore.

To demonstrate the suitability of the joining technique, some joints were made between pieces of a silicon carbide composite material (Figure 1). Joining pieces directly or between the outer coating of silicon carbide was equally successful and no evidence of a deleterious reaction between the joint material and the composite was observed, despite the high-temperature used to melt the pure silicon infiltrant. Apparently, these composite materials are not affected by exposure to the liquid silicon during the short infiltration time.

The microstructure of a joint between two pieces of monolithic silicon carbide is shown in Figure 2. The image shown in Figure 2a shows that the joint region contains an excess of silicon relative to

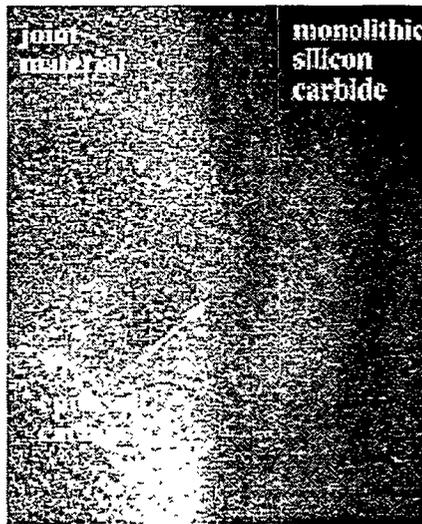


Figure 3. High resolution transmission electron micrograph indicating the presence of carbon with an epitaxial relationship to the monolithic silicon carbide in untreated joints.

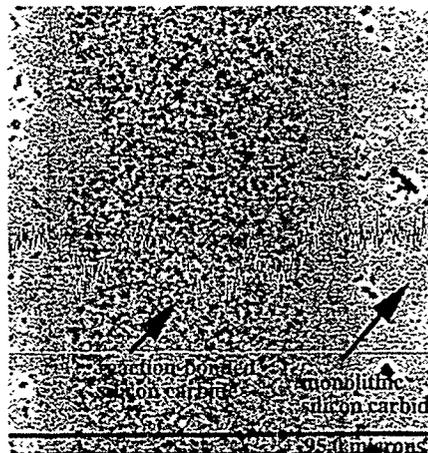


Figure 4. Scanning electron micrograph, with EDX spectra from silicon superimposed, of a cross section of two pieces of monolithic silicon carbide joined by reaction-bonded silicon carbide after annealing for ten cycles to 1100 C.

the monolithic material. This silicon may be silicon that did not react completely during the joint fabrication process. A low resolution transmission electron microscope (TEM) image, Fig. 2b, indicates that the joint material is actually a mixture of three phases: carbon, silicon carbide, and porosity. The porosity may be an artifact of ion thinning. These phases were identified from selected area diffraction patterns. It should be noted that the particle size of the carbon and the reaction-formed silicon carbide are extremely small; i.e., a few hundred nanometers.

It appears that in addition to unreacted silicon in the joint there is also unreacted carbon. Although TEM observations were only limited to the interface between the reaction-bonded silicon carbide and the monolithic silicon carbide, close examination of the EDX spectra of an untreated joint indicates a slight decrease in the silicon signal in the joint near the interface. This suggests that carbon may segregate to the interface region. As shown in Figure 3, carbon particles in an epitaxial relationship with the monolithic silicon carbide were found via HRTEM.

Experiments were conducted to investigate the long term stability of the reaction-formed joint material at elevated temperatures. Several specimens were annealed in a treatment that involved heating the specimens from 25 C to 1100 C in 55 min, holding the temperature at 1100 C for ten hours, rapidly cooling the specimens to 25 C (about 30 min), and repeating this cycle until the specimen had been subject to ten hold periods. Initial SEM microscopy and EDX results, Figure 4, indicates that after this treatment the silicon signal across a typical cross section of a joint is relatively constant. In addition, the appearance of the joint material near the interface with the monolithic silicon carbide is different from that in the middle of the joint. It is possible that further reactions between unreacted silicon and the extremely fine-grained carbon in the untreated joints occurred during annealing. Further microscopy will be conducted to investigate this hypothesis.

## CONCLUSIONS

Preliminary studies have shown that joints between silicon carbide and silicon carbide composites can be fabricated by a reliable, low-cost reaction-forming technique. Annealing appears to promote further reaction-forming between unreacted silicon and carbon. Additional work is required to characterize the microstructure and mechanical properties of untreated and annealed joints.

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